

Structural Refinement of the High-Pressure Phase of Aluminum Trihydroxide: In-Situ High-Pressure Angle Dispersive Synchrotron X-ray Diffraction and Theoretical Studies

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In-situ high-pressure synchrotron angle-dispersive X-ray diffraction for gibbsite (aluminum trihydroxide) was performed at room temperature up to 20 GPa. A pressure-induced phase transition was observed at 2.6 GPa. The new high-pressure phase can be recovered at ambient pressure. Rietveld refinement shows that the new phase of $\text{Al}(\text{OH})_3$ has an orthorhombic structure, spacegroup $Pbca$, and the lattice parameters at ambient condition are $a = 868.57(5)$ pm, $b = 505.21(4)$ pm, $c = 949.54(6)$ pm, $V = 416.67(6) \times 10^6$ pm³ with $Z = 8$. The compressibility of gibbsite and the high-pressure polymorph was analyzed, and their bulk moduli were estimated as 49.8 ± 1.8 and 81.0 ± 5.2 GPa, respectively. First-principles calculations of the high-pressure phase were performed to determine the hydrogen positions and to confirm the structural stability of the new phase.

1. Introduction

Aluminum trihydroxide has been known by humans for over a century, and it is used as a main component of everyday antacid drugs to relieve heartburn and stomach upset. In industry, it is used as an absorbent in chromatography and manufacturing of glass, paper, inks, ceramics, lubricants, cosmetics, etc. The structure and stability of aluminum trihydroxides remain an active subject of investigation, especially by recently developed highly accurate theoretical methods.^{1–4} Four polymorphs, that is, gibbsite (space group $P2_1/n$), bayerite (space group $P2_1/a$), nordstrandite (space group $P1$), and doyleite (space group $P\bar{1}$), have been found in nature.^{5–9} Gibbsite is one of the most abundant natural minerals in the aluminum hydroxide and oxide families, and it was named in 1822 after American collector George Gibbs (1776–1833). Very recently, a new phase of $\text{Al}(\text{OH})_3$ was found from the in-situ high-pressure energy-dispersive X-ray diffraction (EDXRD) experiments using gibbsite as starting material.¹⁰ This new phase was indexed as orthorhombic symmetry, but the structure is unknown due to the lack of intensity information on the diffraction peaks and the low resolution in high-pressure EDXRD spectra. In this report, detail structural information on the new phase of $\text{Al}(\text{OH})_3$ is obtained from Rietveld refinement of in-situ angle dispersive X-ray diffraction (ADXRD) patterns, obtained under high pressure in a diamond anvil cell with high intensity X-ray synchrotron radiation. First-principles calculations were per-

formed to verify the stability of the new phase and to determine the hydrogen positions in the unit cell. The results reported here enrich the understanding of the structures and properties of the aluminum hydroxide family from both a mineralogical and a solid-state chemistry point of view by bringing important experimental data with first-principle calculations and simulations revealing the competition between the known phases of $\text{Al}(\text{OH})_3$ and this higher symmetry new phase under compression conditions.

2. Experimental Section

2.1. Experimental Method. Angle dispersive X-ray diffraction (ADXRD) experiments were carried out at the HPCAT, Advanced Photon Source, Argonne National Laboratory. Synchrotron X-ray ($\lambda = 0.4246$ Å) obtained from a Si (220) monochromator was focused to 20 μm in diameter by a K-B mirror. A T301 stainless steel gasket with a hole diameter of about 100 μm was used as the sample chamber in a diamond anvil cell (DAC). The synthetic gibbsite powder sample and several ruby chips were loaded in the sample chamber, with a methanol–ethanol (4:1) mixture as a pressure-transmitting medium. The pressure was calibrated by the ruby luminescence method.¹¹ Diffraction patterns were recorded on a MAR345 image plate and then integrated by using the program FIT2D.¹²

2.2. Computational Method. First-principles electronic structure calculations were performed with the localized basis set pseudopotential method as implemented in the code SIESTA.^{13,14} The generalized gradient Perdew–Burke–Ernzerhof exchange correlation potentials were employed in the calculations.¹⁵ Valence double- ζ basis sets augmented with polarization functions were used. A plane wave basis set with an energy cutoff of 300 Ry was used in the evaluation Coulomb and exchange-correlation potentials. Full geometry optimization

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TABLE 1: Comparison of the Calculated and Experimental Structural Properties of the New Phase of $\text{Al}(\text{OH})_3$ at Ambient Conditions^a

	calculated	experimental
<i>a</i>	8.783	8.6857(5)
<i>b</i>	5.105	5.0521(4)
<i>c</i>	9.309	9.4954(6)
<i>V</i>	417.4	416.67(6)
Al	(0.3348, 0.0345, 0.9857)	(0.3326, 0.0140, 0.9947)
O ₁	(0.9816, 0.6360, 0.8869)	(0.9810, 0.6394, 0.8952)
O ₂	(0.3018, 0.7334, 0.8665)	(0.2981, 0.7221, 0.9006)
O ₃	(0.8300, 0.1387, 0.9088)	(0.8201, 0.1453, 0.8925)
H ₁	(0.9573, 0.8260, 0.8928)	
H ₂	(0.3877, 0.6600, 0.8110)	
H ₃	(0.8048, 0.1696, 0.8062)	

^a Spacegroup *Pbca*. Lattice constants are in Å, *V* is the unit cell volume in Å³, and (*x*, *y*, *z*) are the fractional atomic coordinates.

TABLE 2: Experimental and Calculated (Marked by *) Lattice Parameters of the New Phase of $\text{Al}(\text{OH})_3$ under Pressure^a

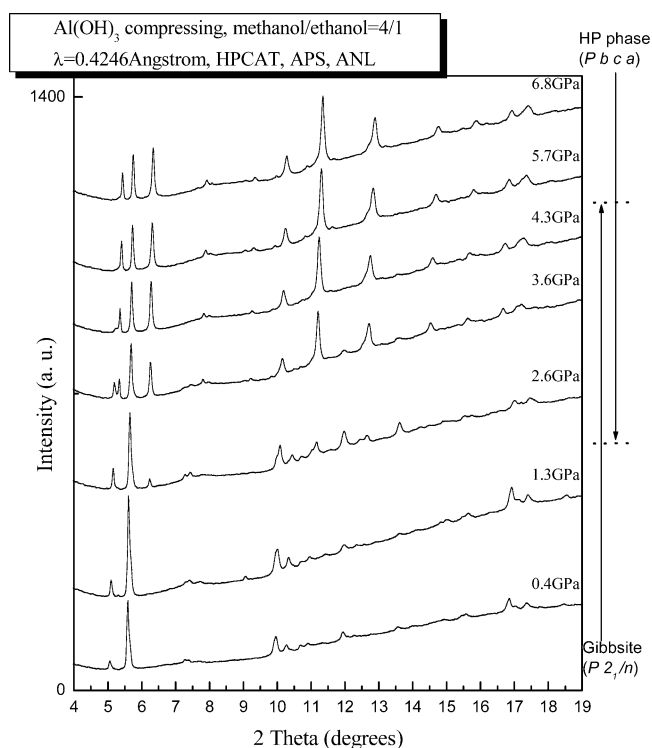
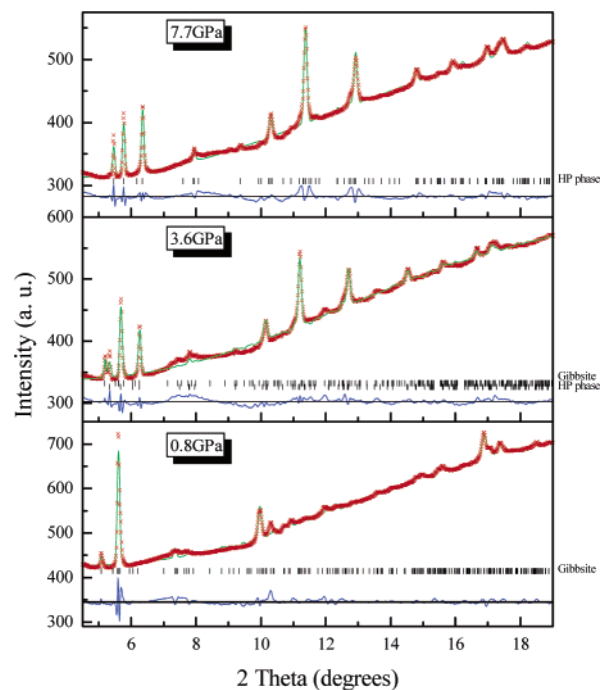
pressure	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>
2.6	8.565(1)	4.979(1)	9.148(2)	390.1(1)
3.1	8.541(1)	4.976(1)	9.127(2)	387.9(1)
3.6	8.520(1)	4.972(1)	9.122(2)	386.4(1)
4.3	8.510(1)	4.960(1)	9.076(2)	383.1(1)
5.0*	8.603*	5.013*	8.995*	388.0*
5.7	8.493(1)	4.935(1)	8.998(2)	377.1(1)
6.8	8.466(1)	4.918(1)	8.948(2)	372.5(1)
7.7	8.444(1)	4.905(1)	8.913(2)	369.2(1)
9.1	8.412(1)	4.886(1)	8.862(2)	364.2(1)
10.3	8.393(1)	4.875(1)	8.831(2)	361.3(1)
13.4	8.361(1)	4.855(1)	8.746(3)	355.1(1)
15.7	8.331(2)	4.836(1)	8.688(3)	350.1(2)
17.8	8.304(2)	4.817(1)	8.646(4)	345.9(2)
19.8	8.278(2)	4.803(1)	8.601(5)	342.0(2)
19.8*	8.303*	4.799*	8.571*	341.5*

^a Pressure is in GPa, lattice constants are in Å, and *V* is the unit cell volume in Å³.

was performed at several selected volumes. The theoretical structural parameters at ambient pressure are compared to the experimental results in Table 1. The agreement between theory and experiment is very satisfactory. The calculated unit cell parameters under compression are also in good accord with the experimental observation as shown in Table 2 and Figure 3.

3. Results and Discussion

Figure 1 shows selected XRD patterns at various pressures. New diffraction peaks start to appear at 2.6 GPa. Upon further compression, the intensity of the new peaks increases, while the peaks intensity of gibbsite diminishes. Above 5.7 GPa, all diffraction peaks from gibbsite phase vanished, indicating that the pressure-induced phase transition has completed. The new high-pressure phase remained stable up to 20 GPa, the highest pressure studied here. The high-pressure phase can be recovered under ambient conditions after the pressure was released. The new phase was found to be orthorhombic.¹⁰ Based on the structural feature of gibbsite, a structure model for the high-pressure phase is proposed. The model has a layered-type structure, in which the layers consist of a similar stacking sequence of ABABAB... as in gibbsite where the AlO_6 octahedra are linked with one shared edge along the *a*–*b* plane. Each oxygen atom is linked to a hydrogen atom. This structure model was found to be correct from the X-ray structural refinement using the GSAS package.¹⁶ Typical Rietveld refined XRD of gibbsite, the coexisting phases, and the high-pressure phase during the phase transition are shown in Figure 2. To the best

**Figure 1.** ADXRD patterns of $\text{Al}(\text{OH})_3$ under compression.**Figure 2.** Typical Rietveld refinement results for gibbsite and the new phase of $\text{Al}(\text{OH})_3$.

of our knowledge, this is the first structural characterization of the new phase.¹⁷

Figure 3 shows the change in lattice parameters of gibbsite and the high-pressure phase as a function of pressure. The orthorhombic structure of the new phase is obtained by transforming the layers in the gibbsite structure by shifting the monoclinic β angle gradually to 90° while keeping other structural features similar to those of gibbsite. Consequently, the spacegroup *P2₁/n* transformed to the supergroup *Pbca*. The bulk modulus (K_0) of gibbsite is estimated as 49.8 ± 1.8 GPa by fitting the *P*–*V* data to the second-order Birch equation of

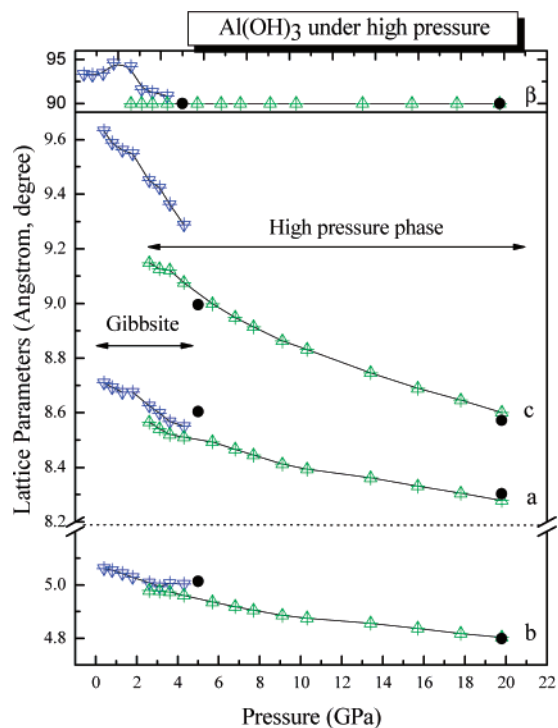


Figure 3. Pressure dependence of lattice parameters of gibbsite and its high-pressure phase. Experimental data were obtained from the compressing process. Calculated parameters are represented by ●. The error bars are omitted because they are smaller than the symbol size.

state.¹⁸ In a similar manner, the bulk modulus of the new phase is estimated as 81.0 ± 5.2 GPa. At ambient conditions, the molar volume of the quenched new phase is about 2% smaller than that of gibbsite.

The hydrogen atom positions could not be detected experimentally because the XRD method provides limited information for light elements. Structure information for hydrogen could be attained from the spectroscopic studies such as Raman and IR, which are sensitive to the change in the hydrogen bonds.^{19,20} The high-pressure IR spectra were measured in-situ up to 25 GPa at room temperature.¹⁰ The results indicated that the six IR active modes in gibbsite reduced to three in the new phase. This observation is in accord with the XRD results in which the high-pressure phase was found to have only three unique oxygen positions. Similar results were observed in the high-pressure Raman experiments,²¹ in which the six Raman active OH stretching modes become three OH stretching modes after the pressure-induced phase transition. The three IR active OH stretching modes of the quenched new phase also help us to evaluate the corresponding hydrogen bond lengths based on the correction of relationship between OH stretching frequencies and hydrogen bond lengths in minerals.²²

First-principles calculations were performed to investigate the structural stability of this new phase and to determine the hydrogen positions. Starting from the Rietveld refined atom positions and assuming that two-thirds of OH groups form interlayer hydrogen bonds to link the layers and one-third of OH groups locate in the intralayer, the structure of the unit cell was fully optimized. Table 1 compares the calculated structural parameters and experimental refinement results at ambient conditions. Figure 4 shows the hydrogen positions in the new phase. The O_1H_1 bonds are located in the layers, forming the intralayer hydrogen bonds. The O_3H_3 bonds are located between layers and form interlayer hydrogen bonds. Finally, the O_2H_2 form tilting interlayer hydrogen bonds. From the theoretical

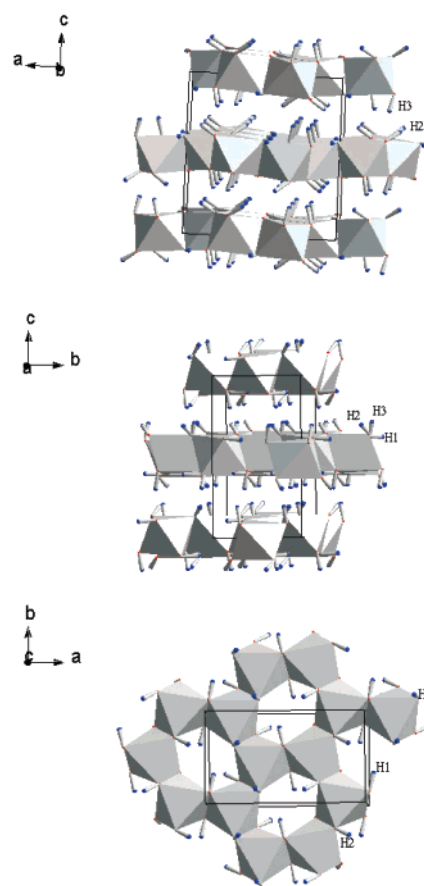


Figure 4. Structure of the new phase of $Al(OH)_3$ with the hydrogen positions from computations.

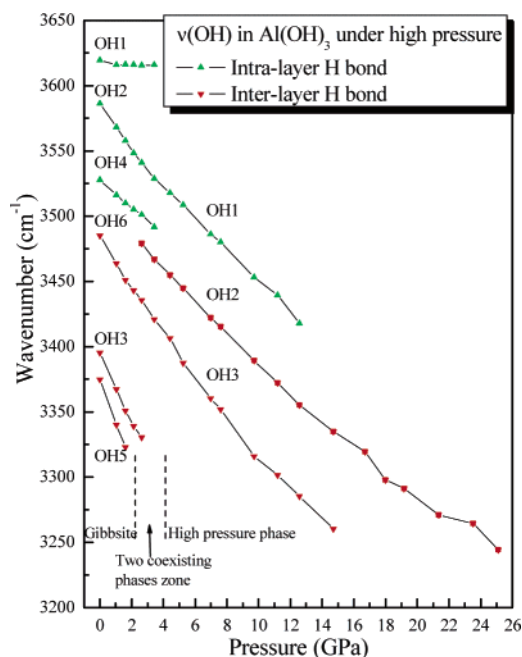


Figure 5. Assignment of the OH stretching modes in high-pressure IR spectra. The assignment for the gibbsite phase is based on previous studies.^{2,19,20}

calculated force field, three OH stretching bands with frequencies of 3317, 3468, and 3513 cm^{-1} were predicted at zero pressure. These values are to be compared to the experimental observed IR bands at 3482, 3512, and 3580 cm^{-1} at ambient condition. Based on experimental structural information and theoretical predictions, we can provide an unambiguous assign-

ment of the OH stretching modes in the high-pressure IR spectra.¹⁰ The results are shown in Figure 5. First-principle calculations also reveal the electronic structure and the role of the hydrogen bond during the phase transition, as well as the detailed change of the hydrogen substructure at higher pressure. Further calculations for the new phase of Al(OH)₃ are in progress, and details will be presented elsewhere.²³

4. Conclusions

In summary, a new phase of Al(OH)₃ was studied by in-situ high-pressure ADXRD. The new phase is orthorhombic space-group *Pbca*, with lattice parameters at ambient conditions of $a = 868.57(5)$ pm, $b = 505.21(4)$ pm, $c = 949.54(6)$ pm, $V = 416.67(6) \times 10^6$ pm³. It has the same layer stacking sequence as the precursor gibbsite and is the highest symmetry structure in the aluminum trihydroxide family. First-principles calculations confirmed the stability of this new phase and determined the hydrogen positions in the unit cell. The assignments of the OH stretching modes in the high-pressure IR spectra were given.

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